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The Electronic Structures of Urazole, Pyrrole, and their Ions. The σ-π Separability Problem

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Ab initio all-electron LCGTO-SCF-MO calculations have been made on the 5-membered ring nitrogen heterocycles urazole ($C_2H_3N_3O_2$), pyrrole (C_4H_5N), and their ion radicals. Wavefunctions were obtained, population analyses made, and electron density contour maps drawn. The results show that for urazole considerable polarity develops in the σ bonds as a result of a large shift of σ charge towards the nitrogen atoms at the expense of the carbon and hydrogen atom σ-electrons with only little effect on the oxygen atom σ charges. In addition, it is concluded that the π-electron approximation should be used with great caution for this type of molecule since the σ-π separability conditions are not well satisfied.

Für die Fünfring-Stickstoffheterocylen Urazol ($C_2H_3N_3O_2$), Pyrrol (C_4H_5N) und ihre Ionenradikale wurden *ab initio* Rechnungen nach der LCGTO-SCF-MO-Methode durchgeführt, wobei alle Elektronen berücksichtigt wurden. Die Besetzungszahlen wurden ermittelt und die Elektronendichten graphisch dargestellt. Die Rechnungen zeigen, daß für Urazol eine beträchtliche Polarität in den σ-Bindungen vorhanden ist. Der Grund dafür liegt in der starken Verschiebung der σ-Ladung in Richtung des Stickstoffatoms auf Kosten der σ-Elektronen des Kohlenstoffs und Wasserstoffs. Die σ-Ladungen am Sauerstoff werden kaum beeinflußt. Von einer π-Elektronenapproximation für diese Art von Molekülen wird abgeraten, da die σ-π-Separationsbedingungen nur ungenügend erfüllt werden.

Calculs *ab-initio* LCGTO-SCF-MO pour tous les électrons des hétérocycles pentagonaux: urazole ($C_2H_3N_3O_2$), pyrrole (C_4H_5N) et de leurs ions-radicaux. Après obtention des fonctions d'onde, l'analyse de population est affectuée et les cartes de densité électronique sont dréssées. Les résultats indiquent que l'urazole présente une forte polarité dans les liaisons sigma résultant d'un transfert de charge sigma vers les atomes d'azote aux dépens des atomes de carbone et d'hydrogène et en affectant peu les atomes d'oxygène. De plus, la séparabilité sigma pi n'est pas bien satisfaite dans ce type de molécule.

1. Introduction

The recent development of high speed computers and sophisticated programming methods have made it possible to produce Hartree-Fock wavefunctions for relatively large atomic and molecular systems with a reasonable expenditure of computer time. Molecules which, heretofore, could be treated only by semiempirical molecular orbital methods, are now susceptible to complete Hartree-Fock treatment.

As a result of the above, it is our intention to analyze the electronic structure of two nitrogen heterocycles, urazole ($C_2H_3N_3O_2$), pyrrole (C_4H_5N), and their ion radicals. At present these are the largest molecules treated to this approximation. In this paper we also examine the validity of the σ-π separability conditions [1],

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involved in π-electron calculation of heterocycles, from a quantitative point of view. The following calculations are reported:

1. Urazole
   a) Ground state,
   b) Cation radical,
   c) Anion radical.
2. Pyrrole
   a) Cation radical,
   b) Anion radical.

The ground state calculation, of comparable accuracy, of pyrrole has been previously reported by Clementi, *et al.* [2].

2. Molecular Parameters

The molecular parameters for urazole are given in Table 1. As there is no reported structural determination for urazole, the molecular parameters are approximated from those of similar molecules for which data is known. Consequently all bond distance were taken from the structure determination of cyanuric acid $(HNCO)_3$ [3]. The nitrogen-nitrogen bond distance was assumed to be 1.35 Å, intermediate between accepted single- and double-bond distances for nitrogen-nitrogen bonds.

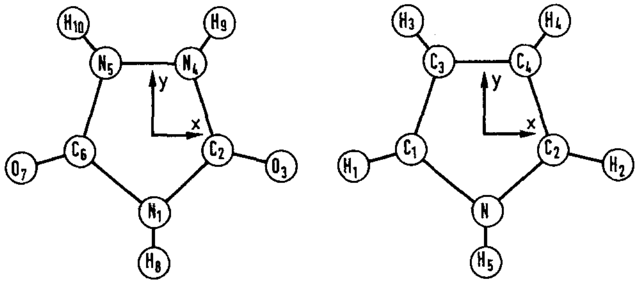
Table 1. *Molecular geometry for urazole*[a]

Center	Cartesian coordinates		
	X	Y	Z
N1	0.0	0.0	0.0
C2	2.163	1.351	0.0
O3	4.329	0.616	0.0
N4	1.275	3.722	0.0
N5	−1.275	3.722	0.0
C6	−2.163	1.351	0.0
O7	−4.329	0.616	0.0
H8	0.0	−1.908	0.0
H9	2.844	4.810	0.0
H10	−2.844	4.810	0.0

[a] Distances are given in atomic units.

The molecule is assumed to be planar with C_{2v} point group symmetry having as the principle axis of symmetry the y-axis. The second axis in the molecular plane is the x-axis, and the axis normal to the plane of the molecule is the z-axis.

The molecular parameters for pyrrole are those reported by Clementi, *et al.* [2]. As in urazole, the principle axis of symmetry is the y-axis, the second axis in the molecular plane is the x-axis, and the z-axis is normal to the plane of the molecule. Molecular diagrams of urazole and pyrrole are given in Fig. 1.



Urazole Pyrrole

Fig. 1. Molecular diagrams for urazole and pyrrole

3. The Basis Set

Due to the difficulty of evaluating many-center integrals over Slater type orbitals, we have chosen a minimal Gaussian type orbital (GTO) basis. Although an expansion of Gaussian functions converges to a Hartree-Fock orbital much slower than an expansion of Slater orbitals, the speed and ease of computation of the many-center integrals over Gaussians overcomes the convergence problem as present computers have ample memory to handle large numbers of basis functions.

Our particular basis set is constructed from special combinations of Gaussian functions, the so-called "contracted Gaussians" as described by Clementi and Davis [4]. The "contracted Gaussian" is a linear expansion of standard GTO's with expansion coefficients obtained from atomic computation with the standard GTO's as a basis. The use of these contracted functions decreases tremendously the order of the energy secular equation.

The standard GTO basis for the urazole calculations consists of 121 Gaussians whose orbital exponents have been optimized for the separated atoms by the method of Huzinaga [5]. The basis of 121 Gaussians is then contracted to a basis of 38 contracted functions. We next transform the contracted Gaussian basis to a set of 38 symmetry-adapted functions. These symmetry-adapted functions for urazole transform as the irreducible representations of the molecular point group C_{2v}. The σ orbitals transform as A_1 and B_2 while the π orbitals transform as B_1 and A_2.

The basis set used for pyrrole is that reported by Clementi [2]. A transformation to our coordinate system will be necessary for proper correlation.

4. The Calculations

The method for the calculation of the molecular wavefunctions is the conventional Hartree-Fock-Roothaan SCF-LCAO-MO method [6]. The calculations were carried out using a program IBMOL, which computes the wavefunctions of atomic and molecular systems using Gaussian orbitals [7]. The computations were made on the IBM System 360 Model 67 computer of the Washington State University Computing Center.

Table 2. *Gross population analysis for the A_1 ground state molecular orbitals of urazole*

	$1a_1$	$2a_1$	$3a_1$	$4a_1$	$5a_1$	$6a_1$	$7a_1$	$8a_1$	$9a_1$	$10a_1$	$11a_1$	$12a_1$	Total
1	−0.0	0.0	1.99291	0.0	0.00082	0.00001	0.00283	0.00033	0.00006	−0.0	0.00005	0.00017	1.99718
2	−0.0	0.99675	0.0	0.0	0.00096	0.00053	0.00070	0.00016	0.0	0.0	0.0	0.00003	0.99913
3	−0.0	0.99675	0.0	0.0	0.00096	0.00053	0.00070	0.00016	0.0	0.0	0.0	0.00003	0.99913
4	−0.0	0.0	0.00808	0.00002	0.28319	0.00027	0.84474	0.11506	0.02181	0.00278	0.00858	0.03752	1.33205
5	−0.0	0.00372	0.0	0.0	0.33684	0.15955	0.22537	0.06048	0.00801	−0.00010	0.00013	0.00422	0.79822
6	−0.0	0.00372	0.0	0.0	0.33684	0.15955	0.22537	0.06048	0.00801	−0.00010	0.00013	0.00422	0.79822
7	0.0	0.0	0.0	0.99892	0.00052	0.00008	0.00002	0.00013	0.00001	0.0	0.0010	0.0	0.99978
8	0.0	0.0	0.0	0.99892	0.00052	0.00008	0.00002	0.00013	0.00001	0.0	0.00010	0.0	0.99978
9	−0.00027	−0.00010	−0.00015	0.00092	0.26501	0.03391	0.01337	0.04646	0.00851	−0.00001	0.04025	−0.00004	0.40786
10	−0.00027	−0.00010	−0.00015	0.00092	0.26501	0.03391	0.01337	0.04646	0.00851	−0.00001	0.04025	−0.00004	0.40786
11	0.99417	0.0	0.0	0.0	0.00049	0.00245	0.00020	0.00004	0.00016	0.00001	0.00085	0.0	0.99837
12	0.99417	0.0	0.0	0.0	0.00049	0.00245	0.00020	0.0004	0.00016	0.00001	0.00085	0.0	0.99837
13	0.00656	−0.0	−0.0	0.00002	0.10651	0.46775	0.03555	0.00672	0.02988	0.00321	0.23697	0.00178	0.89495
14	0.00656	−0.0	−0.0	0.00002	0.10651	0.46775	0.03555	0.00672	0.02988	0.00321	0.23697	0.00178	0.89495
15	−0.0	−0.0	−0.00022	−0.00001	0.00970	−0.00091	0.07071	0.17440	0.03940	0.32487	0.00645	0.01327	0.63766
16	−0.0	−0.00014	−0.0	−0.00001	0.01357	0.00824	0.02114	0.03563	0.13167	0.07572	0.00385	0.00031	0.28998
17	−0.0	−0.00014	−0.0	−0.00001	0.01357	0.00824	0.02114	0.03563	0.13167	0.07572	0.00385	0.00031	0.28998
18	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
19	0.0	−0.00006	−0.0	0.00001	0.01343	0.02951	0.00791	0.08285	0.66727	0.01752	0.02018	0.03185	0.87047
20	0.0	−0.00006	−0.0	0.00001	0.01343	0.02951	0.00791	0.08285	0.66727	0.01752	0.02018	0.03185	0.87047
21	−0.00043	−0.00003	−0.00017	0.0	0.01343	0.19218	0.13487	0.01185	0.00271	0.02628	0.05003	0.00431	0.43503
22	−0.00043	−0.00003	−0.00017	0.0	0.01343	0.19218	0.13487	0.01185	0.00271	0.02628	0.05003	0.00431	0.43503
23	0.00001	−0.0	0.0	0.00008	0.02312	0.04333	−0.00072	0.00044	0.00236	0.00010	0.59315	0.03831	0.70018
24	0.00001	−0.0	0.0	0.00008	0.02312	0.04333	−0.00072	0.00044	0.00236	0.00010	0.59315	0.03831	0.70018
25	−0.0	−0.0	0.0	0.00004	0.04911	0.00391	0.00070	0.38389	0.08042	0.71286	−0.00003	0.05143	1.28233
26	−0.0	0.0	−0.0	0.00002	0.04274	0.00126	0.00144	0.31257	0.02453	0.22955	0.00387	0.05886	0.67484
27	−0.0	0.0	−0.0	0.00002	0.04274	0.00126	0.00144	0.31257	0.02453	0.22955	0.00387	0.05886	0.67484
28	−0.00005	−0.00013	−0.00006	0.0	0.00396	0.05530	0.09777	0.09236	0.03563	0.08785	0.03206	0.00218	0.40687
29	−0.00005	−0.00013	−0.00006	0.0	0.00396	0.05530	0.09777	0.09236	0.03563	0.08785	0.03206	0.00218	0.40687
30	0.0	0.0	0.0	0.00001	0.00301	0.00426	0.00290	0.01347	0.01841	0.03961	0.01101	0.80700	0.89968
31	0.0	0.0	0.0	0.00001	0.00301	0.00426	0.00290	0.01347	0.01841	0.03961	0.01101	0.80700	0.89968
	1.99998	2.00002	2.00001	1.99999	2.00000	1.99998	2.00002	2.00000	1.99999	1.99999	1.99995	2.00001	

Table 3. *Gross population analysis for the B_2 ground state molecular orbitals of urazole*

	$1b_2$	$2b_2$	$3b_2$	$4b_2$	$5b_2$	$6b_2$	$7b_2$	$8b_2$	$9b_2$	Total
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	-0.0	0.99645	0.0	0.00010	0.00130	0.00013	0.00006	0.00002	0.00006	0.99812
3	-0.0	0.9965	0.0	0.00010	0.00130	0.00013	0.00006	0.00002	0.00006	0.99812
4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	-0.0	0.00387	0.00001	0.03661	0.37739	0.04136	0.02968	0.00236	0.01147	0.50275
6	-0.0	0.00387	0.00001	0.03661	0.37739	0.04136	0.02968	0.00236	0.01147	0.50275
7	0.0	0.0	0.99886	0.00050	0.00013	0.00025	0.0004	0.00004	0.0	0.99982
8	0.0	0.0	0.99886	0.00050	0.00013	0.00025	0.00004	0.00004	0.0	0.99982
9	-0.00027	-0.00007	0.00094	0.23046	0.06984	0.12257	0.01546	0.01007	—0.00017	0.44883
10	-0.00027	-0.00007	0.00094	0.23046	0.06984	0.12257	0.01546	0.01007	-0.00017	0.44883
11	0.99414	0.0	0.0	0.00260	0.00057	0.00021	0.0	0.00080	-0.0	0.99832
12	0.99414	0.0	0.0	0.00260	0.00057	0.00021	0.0	0.00080	-0.0	0.99832
13	0.00662	0.0	0.00003	0.51689	0.09643	0.03589	0.00095	0.23338	0.00015	0.89034
14	0.00662	0.0	0.00003	0.51689	0.09643	0.03589	0.00095	0.23338	0.00015	0.89034
15	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
16	0.0	-0.00008	-0.0	0.00053	0.05960	0.04989	0.19530	0.00222	0.02251	0.32997
17	0.0	-0.00008	-0.0	0.00053	0.05960	0.04989	0.19530	0.00222	0.02251	0.32997
18	0.0	0.0	0.00009	0.04110	0.03101	0.74738	0.11413	0.01473	0.19327	1.14171
19	0.0	-0.00008	0.0	0.01375	0.12661	0.03815	0.03196	0.00177	-0.00020	0.21196
20	0.0	-0.00008	0.0	0.01375	0.12661	0.03815	0.03196	0.00177	-0.00020	0.21196
21	-0.00045	-0.00001	-0.00001	0.08850	0.08254	0.14991	0.00253	0.11682	0.00100	0.44083
22	-0.00045	-0.00001	-0.00001	0.08850	0.08254	0.14991	0.00253	0.11682	0.00100	0.44083
23	0.00001	-0.0	0.00008	0.06721	0.00004	0.02239	0.00197	0.50716	0.13043	0.72929
24	0.00001	-0.0	0.00008	0.06721	0.00004	0.02239	0.00197	0.50716	0.13043	0.72929
25	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
26	-0.0	0.0	0.00004	0.01067	0.02782	0.05072	0.36451	0.01666	0.05103	0.52145
27	-0.0	0.0	0.00004	0.01067	0.02782	0.05072	0.36451	0.01666	0.05103	0.52145
28	-0.00005	-0.00008	0.0	0.00224	0.14224	0.09944	0.20134	0.00492	0.00126	0.45131
29	-0.00005	-0.00008	0.0	0.00224	0.14224	0.09944	0.20134	0.00492	0.00126	0.45131
30	0.0	0.0	0.00001	0.00939	-0.00001	0.01544	0.09912	0.09641	0.68581	0.90617
31	0.0	0.0	0.00001	0.00939	-0.00001	0.01544	0.09912	0.09641	0.68581	0.90617
	2.00000	2.00000	2.00001	2.00000	2.00001	2.00008	1.99997	1.99999	1.99997	

Table 4. *Gross population analysis for the A_2 and B_1 ground state molecular orbitals of urazole*

	$1b_1$	$2b_1$	$3b_1$	Total		$1a_2$	$2a_2$	Total
32	0.36980	0.63819	0.73580	1.74279	32	0.0	0.0	0.0
33	0.43376	0.51728	0.00663	0.95767	33	0.18581	0.66493	0.85074
34	0.43376	0.51728	0.00663	0.95767	34	0.18581	0.66493	0.85074
35	0.31827	0.07731	0.04631	0.44189	35	0.47003	−0.00006	0.46997
36	0.31827	0.07731	0.04631	0.44189	36	0.47003	−0.00006	0.46997
37	0.06307	0.08632	0.57916	0.72855	37	0.34416	0.33513	0.67929
38	0.06307	0.08632	0.57916	0.72855	38	0.34416	0.33513	0.67929
	2.00000	2.00001	2.00000			2.00000	2.00000	

5. Ground State Results for Urazole

The ground state electronic configuration for urazole is as follows:

$$\sigma_{a_1} = 1a_1^2\,2a_1^2 \ldots 11a_1^2\,12a_1^2\,,$$
$$\sigma_{b_2} = 1b_2^2\,2b_2^2 \ldots 8b_2^2\,9b_2^2\,,$$
$$\pi_{b_1} = 1b_1^2 2b_1^2 3b_1^2$$
$$\pi_{a_2} = 1a_2^2\,2a_2^2\,.$$

The analysis of the wavefunction for the urazole state is made in two ways: one by considering the results of a Mulliken population analysis [8], and secondly, by inspection of electron density contour maps.

Tables 2–4 give the partial gross populations of the contracted functions (atomic orbitals) in each molecular orbital for the ground state of urazole. Of these, the $5a_1$ molecular orbital, being the first molecular orbital after the ones representing 1*s* atomic orbitals on the heavy atoms, is of particular interest since it is constructed mainly from the 2*s* orbitals of the heavy atoms in the ring. There appears to be considerable delocalization of charge in this lowest σ bonding

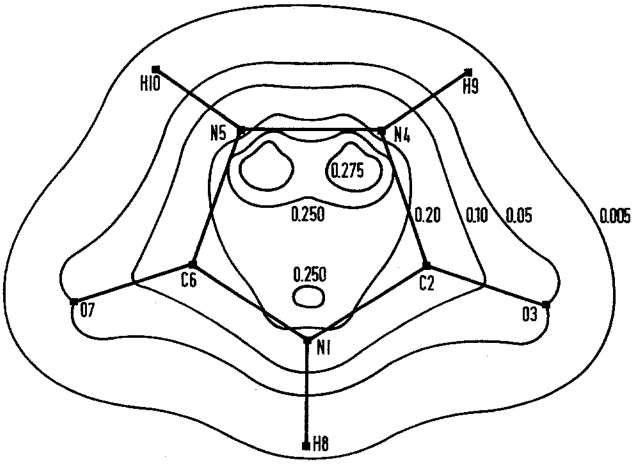


Fig. 2. Electron density map for the $5a_1$ molecular orbital of the ground state of urazole in the molecular plane

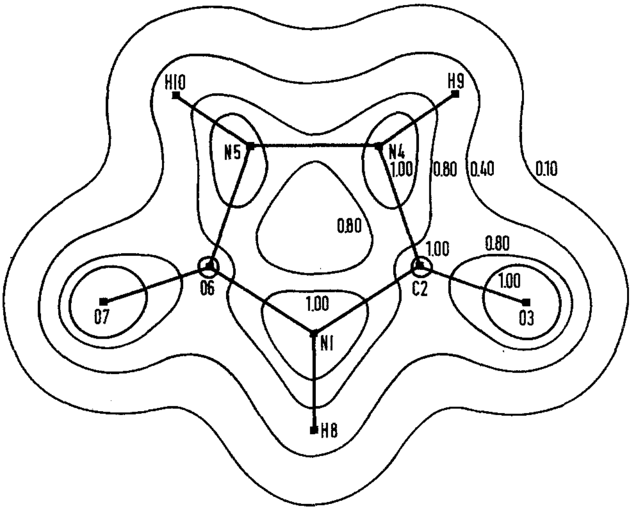


Fig. 3. Electron density map for the total σ molecular orbital system of the ground state of urazole in the molecular plane

molecular orbital. The electron density contour map for the $5a_1$ molecular orbital is given in Fig. 2. The bulk of the electron density is found within the ring, primarily in the vicinity of the nitrogen atoms, however there is strong evidence here for considerable delocalization.

The set of σ molecular orbitals, $11a_1$, $12a_1$, $8b_2$, and $9b_2$ may be attributed to the "lone-pair" orbitals of the carbonyl oxygens. The $11a_1$ and $8b_2$ molecular orbitals have O(2s) and O($2p_x$) character which strongly indicate digonal hybrids.

Table 5. *Orbital populations for urazole*

	G.S.	Cation	Anion		G.S.	Cation	Anion
1 N1(1*s*)	1.99718	1.99722	1.99724	20 N5(*x*)	1.08242	1.13964	1.05410
2 N4(1*s*)	1.99724	1.99773	1.99712	21 C2(*x*)	0.87588	0.85307	0.85741
3 N5(1*s*)	1.99724	1.99773	1.99712	22 C6(*x*)	0.87588	0.85307	0.85741
4 N1(2*s*)	1.33206	1.33975	1.34080	23 O3(*x*)	1.42947	1.45795	1.43669
5 N4(2*s*)	1.30097	1.40078	1.28124	24 O7(*x*)	1.42947	1.45795	1.43669
6 N5(2*s*)	1.30097	1.40078	1.28124	25 N1(*y*)	1.28232	1.33347	1.23259
7 C2(1*s*)	1.99961	1.99927	1.99931	26 N4(*y*)	1.19627	1.38635	1.18305
8 C6(1*s*)	1.99961	1.99927	1.99931	27 N5(*y*)	1.19627	1.38635	1.18305
9 C2(2*s*)	0.85671	0.79291	0.84002	28 C2(*y*)	0.85819	0.73644	0.82871
10 C6(2*s*)	0.85671	0.79291	0.84002	29 C6(*y*)	0.85819	0.73644	0.82871
11 O3(1*s*)	1.99669	1.99684	1.99651	30 O3(*y*)	1.80586	1.79148	1.79702
12 O7(1*s*)	1.99669	1.99684	1.99651	31 O7(*y*)	1.80586	1.79148	1.79701
13 O3(2*s*)	1.78527	1.80615	1.76227	32 N1(*z*)	1.74379	1.65777	1.70756
14 O7(2*s*)	1.78527	1.80615	1.76227	33 N4(*z*)	1.80841	1.24013	1.90217
15 H8(1*s*)	0.63766	0.57019	0.72006	34 N5(*z*)	1.80841	1.24013	1.90217
16 H9(1*s*)	0.61994	0.45610	0.71835	35 C2(*z*)	0.91186	1.23718	1.15062
17 H10(1*s*)	0.61994	0.45610	0.71835	36 C6(*z*)	0.91186	1.23718	1.15062
18 N1(*x*)	1.14171	1.12997	1.20586	37 O3(*z*)	1.40784	1.19380	1.59354
19 N4(*x*)	1.08242	1.13964	1.05410	38 O7(*z*)	1.40784	1.19380	1.59354

Table 6. *Net charges for urazole*

		[12,9,3,2]	Cation	Anion
N1	$\delta\sigma$	−0.75327	−0.80041	−0.77649
	$\delta\pi$	+0.25621	+34223	+0.29244
	δ	−0.49706	−0.45818	−0.48405
C2	$\delta\sigma$	+0.40961	+0.61831	+0.47456
	$\delta\pi$	+0.08814	−0.23718	−0.15062
	δ	+0.49775	+0.38113	+0.32394
O3	$\delta\sigma$	−0.01729	−0.05242	+0.00751
	$\delta\pi$	−0.40784	−0.19380	−0.59354
	δ	−0.42513	−0.24622	−0.58603
N4	$\delta\sigma$	−0.57690	−0.92450	−0.51551
	$\delta\pi$	+0.19159	+0.75987	+0.09793
	δ	−0.38531	−0.16463	−0.41758
H8	δ	+0.36234	+0.42981	+0.27994
H9	δ	+0.38006	+0.54390	+0.28165
Total energy		−338.21540	−387.48891	−388.06987

The $12a_1$ and $9b_2$ molecular orbitals are nearly pure $O(2p_y)$, indicating pure *p*-type lone-pairs. On the basis of this, one could describe the hybridization of the carbonyl oxygens as $di^2 di\, p^2\pi$.

The total σ electron density map is given in Fig. 3. It is evident from this figure that there is a considerable redistribution of the σ charge on binding. This redistribution can be anticipated by a consideration of the electronegativities of the heavy atoms. The density map shows an extremely large shift of σ charge toward the nitrogens. This shift is at the expense of the carbons and hydrogens. There is

Table 7. *Urazole energy eigenvalues*

A_1	[12,9,3,2]	Cation	Anion	B_2	[12,9,3,2]	Cation	Anion
1	−20.370785	−20.658853	−19.996706	1	−20.370799	−20.658866	−19.996722
2	−15.749676	−16.184911	−15.446036	2	−15.740317	−16.184335	−15.440882
3	−15.705465	−15.923931	−15.441190	3	−11.624307	−11.804288	−11.261038
4	−11.624272	−11.804224	−11.260973	4	− 1.453557	− 1.693337	− 1.147733
5	− 1.548588	− 1.850545	− 1.259077	5	− 1.213005	− 1.519223	− 0.927300
6	− 1.402936	− 1.658203	− 1.101880	6	− 0.941478	− 1.181425	− 0.655120
7	− 1.289497	− 1.528563	− 1.018114	7	− 0.728759	− 1.016386	− 0.461373
8	− 0.926288	− 1.237978	− 0.667722	8	− 0.634210	− 0.868234	− 0.343293
9	− 0.882741	− 1.210169	− 0.464516	9	− 0.472981	− 0.718981	− 0.182279
10	− 0.723172	− 0.959678	− 0.464516				
11	− 0.646996	− 0.880075	− 0.358653				
12	− 0.508809	− 0.758805	− 0.216957				

B_1	[12,9,3,2]	Cation	Anion	A_2	[12,9,3,2]	Cation	Anion
1	− 0.786088	− 1.045929	− 0.520448	1	− 0.638312	− 0.847031	− 0.366103
1	− 0.601037	− 0.834979	− 0.344395	2	− 0.404030	− 0.366149	− 0.155211
3	− 0.464298	− 0.643048	− 0.201515	3			+ 0.658158
4							

surprisingly little effect on the oxygen σ charge. All of this evidence strongly indicates a tendency for ease of delocalization of σ charge. Clementi's results for pyrrole indicate a similar tendency [2].

From the first column of Table 7 we see that there are three π molecular orbitals with energy lower than the highest σ molecular orbitals, however, only the $1b_1$ lies lower than a σ bonding molecular orbital if the $11a_1$, $12a_1$, $8b_2$, and $9b_2$ orbitals are considered to be lone-pair non-bonding orbitals. This is contrary to the popular belief that the π molecular orbitals all lie above the σ molecular orbitals in energy, which may be an indication of the difficulties in σ-π separability.

6. σ-π Separability

In this section we discuss an investigation of the molecular orbital rearrangements which occur in a heterocyclic molecule when a change is made in the configuration of the π-electronic system. The primary objective is to examine the basic assumption of π-electron theory, that the σ portion of the molecular wavefunction remains unaltered by a change in the π portion of the wavefunction. The σ electronic reorganization for a gain or loss of a π-electron should be an indicator of the validity of the π-electron approximation. The following configurations of urazole and pyrrole are calculated and compared:

$$\begin{array}{lll}
\text{Ground State } \pi & = 1b_1^2\, 2b_1^2\, 3b_1^2\, 1a_2^2\, 2a_2^2 & \text{(urazole)}, \\
\pi & = 1b_1^2\, 2b_1^2\, 1a_2^2 & \text{(pyrrole)}, \\
\text{Cation} \quad \pi' & = 1b_1^2\, 2b_1^2\, 3b_1^2\, 1a_2^2\, 2a_2^1 & \text{(urazole)}, \\
\pi' & = 1b_1^2\, 2b_1^2\, 1a_2^1 & \text{(pyrrole)}, \\
\text{Anion} \quad \pi'' & = 1b_1^2\, 2b_1^2\, 3b_1^2\, 1a_2^2\, 2a_2^2\, 3a_2^1 & \text{(urazole)}, \\
\pi'' & = 1b_1^2\, 2b_1^2\, 3b_1^1\, 1a_2^2 & \text{(pyrrole)}.
\end{array}$$

Table 8. *Orbital populations for pyrrole*

	G.S.	Cation	Anion		G.S.	Cation	Anion
1 N(1*s*)	1.99752	1.99751	1.99729	16 N(*x*)	1.14364	1.08781	1.15343
2 N(2*s*)	1.37038	1.38071	1.33496	17 C1(*x*)	1.02115	1.12505	0.93042
3 C1(1*s*)	1.9918	1.9936	1.99887	18 C2(*x*)	1.02115	1.12505	0.93042
4 C1(2*s*)	1.04728	1.11206	0.98491	19 C3(*x*)	1.03068	1.05721	1.01243
5 C2(1*s*)	1.99918	1.99936	1.99887	20 C4(*x*)	1.03068	1.05721	1.01243
6 C2(2*s*)	1.04728	1.11206	0.98491	21 N(*y*)	1.23622	1.28662	1.14319
7 C3(1*s*)	1.99908	1.99912	1.99898	22 C1(*y*)	0.96328	0.99550	0.92929
8 C3(2*s*)	1.05559	1.09006	1.03239	23 C2(*y*)	0.96328	0.99550	0.92929
9 C4(1*s*)	1.99908	1.99912	1.99898	24 C3(*y*)	1.07377	1.10127	1.04555
10 C4(2*s*)	1.05559	1.09006	1.03239	25 C4(*y*)	1.07377	1.10127	1.04555
11 H1(1*s*)	0.79835	0.66598	0.93992	26 N(*z*)	1.65903	1.64507	1.79925
12 H2(2*s*)	0.79835	0.66598	0.93992	27 C1(*z*)	1.07498	0.73007	1.39096
13 H3(1*s*)	0.80748	0.69222	0.92079	28 C2(*z*)	1.07498	0.73007	1.39096
14 H4(1*s*)	0.80748	0.69222	0.92079	29 C3(*z*)	1.09556	0.94741	1.20941
15 H5(1*s*)	0.66059	0.57154	0.78397	30 C4(*z*)	1.09556	0.94741	1.20941

Table 9. *Net charges for pyrrole*

		[9, 6, 2, 1]	Cation	Anion
N	$\delta\sigma$	−0.74776	−0.75265	−0.62887
	$\delta\pi$	+0.34097	+0.35493	+0.20075
	δ	−0.40679	−0.39772	−0.42812
C 1	$\delta\sigma$	−0.03088	−0.23197	+0.15651
	$\delta\pi$	−0.07493	+0.26993	−0.39096
	δ	−0.10581	+0.03796	−0.23445
C 3	$\delta\sigma$	−0.15912	−0.24766	−0.08935
	$\delta\pi$	−0.09556	+0.05259	−0.20941
	δ	−0.25468	−0.19507	−0.29876
H 1	δ	+0.20165	+0.33402	+0.06001
H 3	δ	+0.19252	+0.30778	+0.07921
H 5	δ	+0.33941	+0.42846	+0.21603
Total energy		−207.93070	−207.56987	−207.81777

To truly study the deformation of the electronic structure, one should look at two types of deformation: (1) Molecular deformation, *i.e.* changes in the molecular orbital coefficient; and (2) Atomic deformation, *i.e.* changes in the orbital exponents and contraction coefficients of the Gaussians. However, since the ground state calculations were made using a "free atom" basis, the ions also were done in this manner. Consequently, we are only studying molecular deformation.

According to the π-electron approximation, if there is a change in the π-system of a molecule, there will be no change in the σ system. If, however, there is an effect on the σ portion of the wavefunction, it will be reflected in the σ molecular orbital energy eigenvalues and also in the molecular orbitals themselves.

A comparison of the orbital energies of the several states of urazole and pyrrole is given in Tables 7 and 10, respectively. The obvious feature of this comparison

Table 10. *Pyrrole energy eigenvalues*

A_1	[9,6,2,1]	Cation	Anion	B_2	[9,6,2,1]	Cation	Anion
1	−15.710376	−15.974391	−15.386195	1	−11.425389	−11.750351	−11.094582
2	−11.425323	−11.750395	−11.095432	2	−11.378825	−11.669481	−11.078803
3	−11.379634	−11.670351	−11.078778	3	− 1.034538	− 1.313399	− 0.751838
4	− 1.324117	− 1.60444	− 1.028931	4	− 0.797092	− 1.060737	− 0.530186
5	− 1.095583	− 1.366003	− 0.821461	5	− 0.623714	− 0.894467	− 0.349660
6	− 0.825425	− 1.078060	− 0.565911	6	− 0.602384	− 0.855422	− 0.344812
7	− 0.777633	− 1.044255	− 0.508084				
8	− 0.647994	− 0.903355	− 0.385032				
9	− 0.576546	− 0.840534	− 0.316159				

B_1	[9,6,2,1]	Cation	Anion	A_2	[9,6,2,1]	Cation	Anion
1	− 0.631467	− 0.876320	− 0.364539	1	− 0.388049	− 0.692197	− 0.131469
2	− 0.425488	− 0.677017	− 0.179247	2			
3			+ 0.767874				

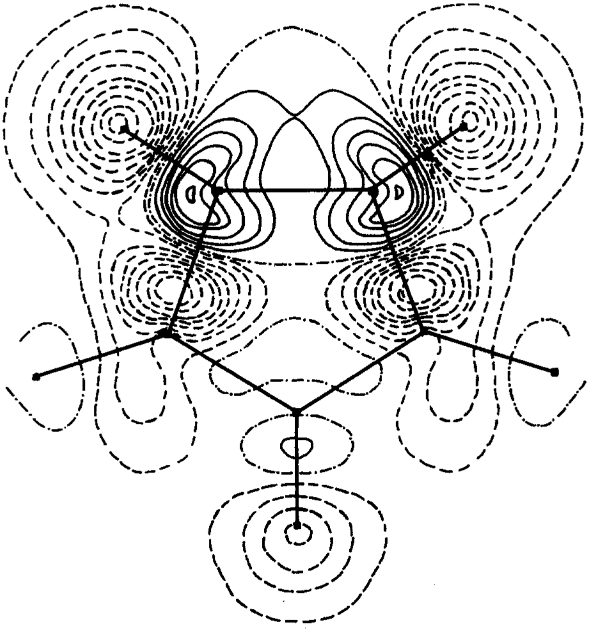


Fig. 4. Difference map of the σ-electron density of the cation of urazole minus the σ-electron density of the ground state of urazole in the molecular plane. Alternating dot-dash lines are zero contours, dashed lines are negative contours, and solid lines are positive contours. Contour increments are 0.01

is that all of the orbital energies of the cations of both molecules are lower than for the ground states, and all of the orbital energies of the anions are higher than in the ground states. This effect can be attributed to increased or decreased $\sigma\pi$ repulsion interactions corresponding to the number of π-electrons.

The reorganization of the σ wavefunctions for urazole and pyrrole are displayed in Tables 5, 6, 8, and 9, which summarize the Mulliken population analyses. The flow of σ electron distribution upon loss or addition of a π-electron can be viewed readily from the electron density difference maps of Figs. 4—7. Figs. 4 and 5 are plots of the σ electron distribution of the cations of urazole and pyrrole, respectively, minus the ground state distributions,

$$\delta(\sigma) = \sum_{\text{cat}}^{*} \sum_{\text{cat}} - \sum_{gs}^{*} \sum_{gs} .$$

Figs. 6 and 7 are plots of the difference between the σ-electron distribution of the anions of urazole and pyrrole, respectively, and the ground state distributions,

$$\delta(\sigma)' = \sum_{\text{an}}^{*} \sum_{\text{an}} - \sum_{gs}^{*} \sum_{gs} .$$

For the cations, the flow of electrons is from the hydrogens to the ring. For urazole, the nitrogens absorb most of the shifting charge, while in pyrrole, the carbon atoms gain the charge. The reduced $\sigma\,\pi$ repulsion for the cations allow the more electronegative ring atoms to take up more of the σ charge. Conversely for the anions, the flow of electrons is toward the hydrogens at the expense of the electron density at or near the ring. The increased $\sigma\pi$ repulsion for the anions would have a more substantial effect on the electron-rich heavy ring atoms and thus would force density away from these positions.

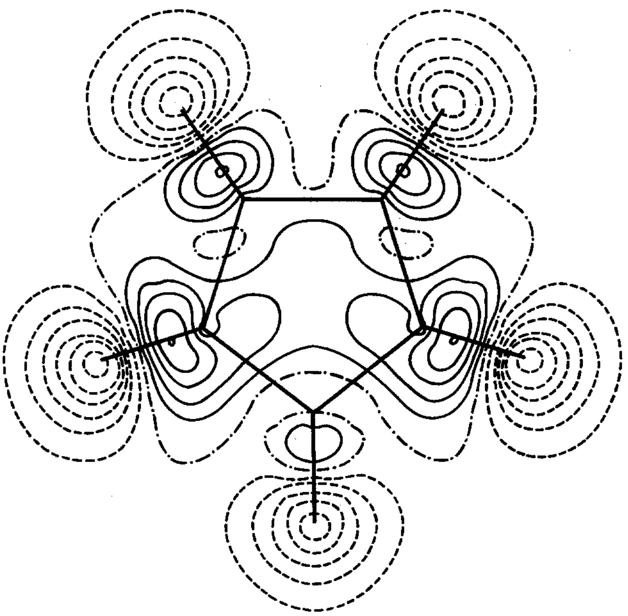


Fig. 5. Difference map of the σ-electron density of the cation of pyrrole minus the σ-electron density of the ground state of pyrrole in the molecular plane. Alternating dot-dash lines are zero contours, dashed lines are negative contours, and solid lines are positive contours. Contour increments are 0.01

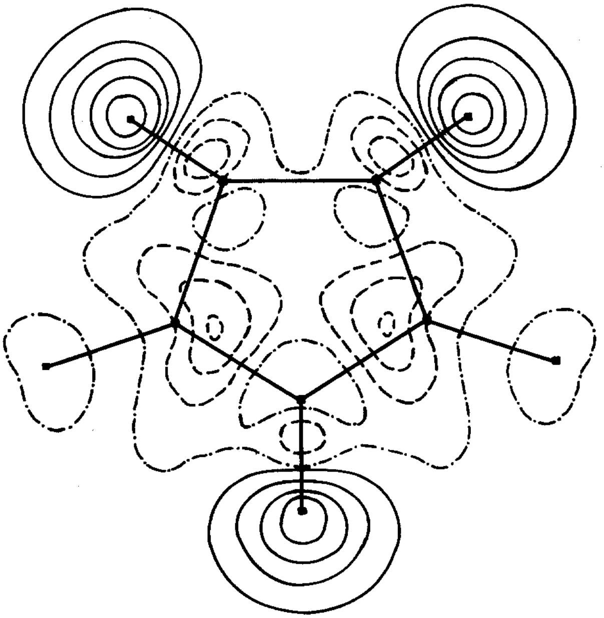


Fig. 6. Difference map of the σ-electron density of the anion of urazole minus the σ-electron density of the ground state of urazole in the molecular plane. Alternating dot-dash lines are zero contours, dashed lines are negative contours, and solid lines are positive contours. Contour increments are 0.01

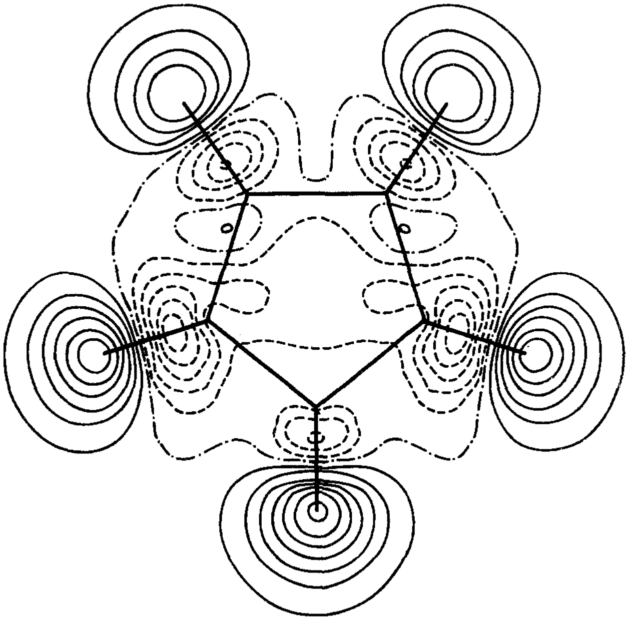


Fig. 7. Difference map of the σ-electron density of the anion of pyrrole minus the σ-electron density of the ground state of pyrrole in the molecular plane. Alternating dot-dash lines are zero contours, dashed lines are negative contours, and solid lines are positive contours. Contour increments are 0.01

Due to increased or decreased $\sigma\pi$ repulsion, as evidenced in the change in the molecular orbitals, the σ electronic system is distorted considerably with the most noticeable effect at the hydrogens. This would have a marked effect on the chemical properties of heterocycles.

As with the σ energy eigenvalues, the changes in π energy eigenvalues reflect principally the number of π-electrons. For the cations, the energy eigenvalues are lower, as would be expected from a $\pi\pi$ repulsion argument. For the anions, the energy eigenvalues are higher, again as expected.

The most important result of the comparison of the relative σ and π distortion is that they are of comparable magnitude. This is strong evidence for questioning the validity of the π-electron approximation.

In addition to the above, the use of Koopmans' theorem [9] for calculating ionization potentials appears to be invalid. The basic tenet of Koopmans' theorem, from the molecular orbital point of view, is that the molecular orbitals are unchanged upon ionization of an electron. It is evident from our results that not only the molecular orbital from which the electron was removed, but also all of the molecular orbitals of the system are considerably altered on ionization. Ignoring differences in correlation energy, we can take the ionization potential to be the difference between the energy of the molecules in their ground states and the energy of their respective cations. For urazole, the Koopmans' theorem ionization potential is 0.40403 au as compared to a calculated 0.72549 au. For pyrrole, the Koopmans' theorem ionization potential is 0.38805 au as compared to a calculated 0.3608 au. The results for pyrrole agree rather closely, but the urazole values differ considerably. The apparent lack of correlation between these values only casts further doubt on the validity of Koopmans' theorem for heterocycles.

7. Conclusions

From the above results, we can affirm, from quantitative arguments, that the π-electron approximation should be used with reservation. As indicated, there is considerable effect on the σ-electronic structure when the π system is changed. The change is most evident in the energy eigenvalues and from the results of population analyses. These conclusions are in qualitative agreement with Clementi's results for pyridine [10].

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